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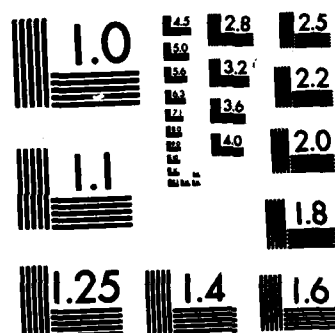
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Mechanistic Studies of Adhesion Promotion by γ -Aminopropyl Triethoxy Silane in α -Al₂O₃/Polyethylene Joint

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In order to understand the mechanism of adhesion promotion by organo silane in joints where its chemical reaction with a polymer matrix may be negligible, we studied the role of γ -aminopropyl triethoxy silane (γ -APS) in α -Al₂O₃/polyethylene joints. When adsorbed or deposited on α -Al₂O₃ and moderately dried, γ -APS forms a multimolecular film that is not fully cured. Drying at elevated temperatures for an extended time leads to further curing, resulting in a glassy silane film with a T_g around 108°C, while prolonged dry may cause some degradation. Joint strength is markedly improved by the application of a γ -APS film with a maximum peel strength of 2.3 kg/cm when the silane is applied from a 2 percent aqueous solution. Drying the silane at an elevated temperature prior to joint formation reduces joint strength and also changes the failure mode from cohesive failure through the polyethylene to a mixed mode. Evidence of interdiffusion between γ -APS film and polyethylene at a temperature (149°C) that is above the melting point of polyethylene and the T_g of the silane film was obtained by measuring the Si concentration profile across the interface of the laminate of polyethylene/ γ -APS/polyethylene. Diffusion constants in the order of 10^{-12} cm²/s were obtained, with a tendency toward reduced diffusion as a consequence of extensive drying. DSC results indicate at least partial miscibility of the silane polymer in the amorphous region of polyethylene. It is proposed that the interdiffusion between γ -APS silane film and polyethylene is an important mechanism for adhesion promotion of the joints investigated in this study.

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INTRODUCTION

Adhesion promoters, which are organometallic compounds, have been used with varying degrees of success to modify the surface of adherends (glass fibers, metals, or metal oxides) prior to bonding with polymers in order to enhance joint strength, especially against a wet environment. The most common type of coupling agent is organo silane having the structure of $X_3\text{Si}(\text{CH}_2)_n\text{Y}$, where X is a hydrolyzable group such as ethoxy, Y is an organofunction group such as amino or vinyl, and n can vary from 0 to 3.

Silane films, when deposited on many substrates, are shown to be polymeric, with a film thickness much greater than the monolayer (1-4). Their composition also

appears to be nonuniform; i.e., they may contain a strongly-held polysiloxane network, along with some hydrolyzed silane and small siloxane molecules. This interpretation was mainly inferred from solvent extraction studies by Schrader (3, 4) and by Bascom (2). More recently, some direct IR spectral evidence has been provided on the nonuniform composition of silane films on glass fibers (5) or iron (6) surfaces.

The exact mechanism for the role of adhesion promoters has been one of the controversial areas in adhesion science. In certain cases, the presence of primary bonding at the silane/substrate interface and/or at the polymer/silane interface may be an important requirement for increasing joint strength. Recent studies have

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provided some direct evidence for the presence of such primary interfacial bonds. For example, Koenig and coworkers (7-9), using laser Raman or IR spectroscopy, have observed the presence of a Si-O-Si bond at the glass/silane interface and of a covalent bond between the amino group of organo silane and the epoxy resin.

While the primary bonding mechanism may explain some of the features of adhesion promotion, several important considerations do not fit a covalent bonding mechanism model. First, certain organofunctional silanes are very good adhesion promoters for inert polymers (e.g., polyolefins) under conditions where chemical reaction is unlikely (10). Secondly, it is well known that the bond of Si-O-Metal (e.g., Al-O-Si) is not particularly stable against a wet environment (11, 12), and yet water-resistant bonds through silanes to aluminum are possible (13). Also, there are several reported cases (14, 15) in which, in spite of the presence of covalent bonds across the interface, poor adhesion and wet strength were observed. It appears, therefore, that some other mechanism may be responsible for adhesion promotion, at least in some cases.

The objective of the work described in this paper has been to identify and to provide support for such an alternative mechanism of adhesion promotion by an organo silane. We chose γ -aminopropyl triethoxy silane (γ -APS) as the adhesion promoter and (unoxidized) polyethylene as the polymer because chemical reaction between them is unlikely and, thus, this would be a joint in which mechanisms other than primary bonding would be important for any adhesion promotion. As for the model substrate, we chose single crystalline alumina (α -Al₂O₃), sapphire, for experimental advantages that have been previously discussed (16).

FT-IR, ESCA, DSC, ellipsometry, SEM, and X-ray fluorescence energy dispersive analysis (SEM-EDX) were utilized to characterize the structure of the deposited bulk silane, interfacial reactions, and the failure locus and mode of the joints. Attempts were then made to correlate structural information with joint strength by measuring 180° peel strength of the sapphire/silane/polyethylene joints.

EXPERIMENTAL

Materials

γ -aminopropyl triethoxy silane (γ -APS) was donated by Union Carbide and used without further purification. Sapphire single-crystal plates (2" × 1" × 0.03") were purchased from Tyco-Saphikon Co. The surface of the sapphire plate is identified as the 1120 plane, which is parallel to the c-axis of the crystal. The sapphire was washed with acetone several times, followed by heat treatment at 350°C for 1 h to remove organic contaminants. The polyethylene was a medium density polymer in the form of a 0.01"-thick calendered film, courtesy of the Kendall Co. As-received polyethylene film was washed with hexane several times to clean contaminants and low molecular weight species.

Infrared Analysis

A Fourier Transform IR spectrometer (FTS-14 or -15, from Digilab) was used to record difference spectra of the deposited silane by subtracting sapphire spectra, usually after 100 or 200 scans at a resolution of 4 cm⁻¹. Details of the sample preparation conditions will be described in the Results section.

ESCA Analysis

A PHI Model 548 Electron Spectrometer, using MgK α radiation as the exciting photons, was used. The pressure inside the sample chamber during the ESCA run was about 10⁻⁸ ~ 10⁻⁹ torr.

SEM and SEM-EDX Analysis

SEM or SEM-EDX analysis was done with a Cambridge Stereoscan Model Mark IIA with gold-coated surfaces. Laminates of polyethylene and silane film made under similar conditions to those of the peel specimen were cut perpendicular to the interface, with care taken not to contaminate the interface. The interface was analysed by SEM-EDX by determining the concentration of Si atoms. The silicon count was collected for 200 s at each position across the interface. The acceleration voltage used in SEM-EDX was 20 KeV.

Peel Strength Sample Preparation and Testing

Cleaned sapphire plates were heated at 350°C in an oven for 1 h to remove organic contaminants and immediately spray-coated on both sides with aqueous γ -APS solutions (pH 10.4) of a given concentration. The sapphire plates were then dried in a vacuum oven under varying drying conditions prior to lamination with polyethylene. The peel specimens were prepared by laminating polyethylene films on both sides of the Al₂O₃ plate under a hot press at 149°C for 15 min. Peel strength of the laminate was measured at room temperature with a 180° peel on each side using a Table Model Instron at a peel rate of 1"/min.

DSC

Glass transition temperatures were measured by employing a Perkin-Elmer differential scanning calorimeter Model DSC-2 at a heating rate of 10°C/min, with about 20 mg of the sample.

Ellipsometry

An ellipsometer from Gaertner Scientific, Model Production Ellipsometer L117, was used to measure the thickness of deposited amino silane film on α -aluminum oxide, according to a method similar to that of Tutas, *et al* (17). Actual thicknesses were calculated using data conversion software from Hewlett-Packard.

RESULTS AND DISCUSSION

In order to understand the role of γ -APS in adhesive joints, it is necessary to determine the structure of the deposited bulk silane, the interfacial interactions, and their relation to adhesive joint strength and failure mode.

Bulk Characterization of Deposited Amino Silane

Our earlier IR studies showed that the silane on sapphire may not be fully cured if it was only slightly dried (16). It is reasonable to expect that the exact structure of the deposited silane would be influenced by the pH of the initial solution, as demonstrated by Boerio and coworkers (6, 13), or by the drying conditions of the deposited film. Further drying at elevated temperatures would likely drive the reactions toward further condensation and cross-linking, as was observed in vinyl-silane by Ishida and Koenig (18). With thick films of γ -APS, similar trends seem to occur as a function of drying time at elevated temperatures. For example, Fig. 1(e) corresponds to that of standard drying conditions, where two strong peaks, at 1570 cm^{-1} and 1480 cm^{-1} , are shown. The 1570 cm^{-1} peak was much smaller in the monomer. Recent studies by Boerio, *et al* (13, 19), suggest that both peaks are due to amino bicarbonate from the reaction of dissolved carbon dioxide and the amine group (20). Since both of these peaks disappear after drying at 110°C , as shown for the rest of Fig. 1, such an assignment appears to be reasonable. Figure 1(d) corresponds to drying at 110°C for 7 min. Here, Si-OH groups at 3400 cm^{-1} are drastically reduced in comparison to Fig.

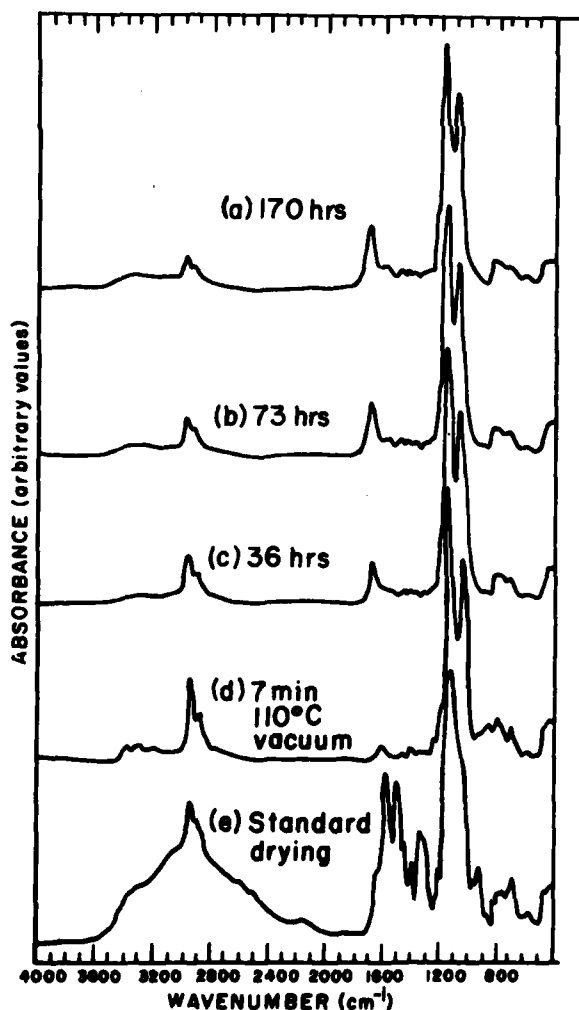


Fig. 1. IR spectra of deposited γ -APS film on KRS-5 crystal as a function of extended drying.

1(e), but Si-O-Si peaks at 1140 cm^{-1} and 1035 cm^{-1} are clearly visible and much more intense than in Fig. 1(e), while peaks for Si-O-C (at 1178 , 1110 , or 1087 cm^{-1}) decrease. With increasing drying time, the intensity of the Si-O-Si peak increases relative to the CH_2 peak at 2930 cm^{-1} . Also noted is the fact that the NH bending peak around 1615 cm^{-1} becomes progressively shifted to a higher wavenumber up to 1670 cm^{-1} after 170 h of drying. This shift may be due either to the association of NH groups with others (21, 22) or to the formation of $-\text{C}=\text{NH}$ as a result of some degradation (21).

Figure 2 shows ESCA spectra obtained on deposited γ -APS on sapphire as a function of the concentration (thickness) of silane and drying conditions. We can observe the following trends from Fig. 2:

- With a thin silane film (low concentration of silane, less than 2 percent), the silane does not cover the sapphire completely, since Al peaks appear from the sapphire substrate.
- After standard drying, an N_{1s} peak occurs at 399 eV. However, this peak is not symmetrical, and there is a small amount of higher energy N_{1s} peak centered around 400 eV, which has been assigned to the N^+ species by Nordberg, *et al* (23). After prolonged drying, the main N_{1s} peak is shifted to 400 eV.

Since the IR spectra clearly show an increase in the Si-O-Si band and a decrease in Si-OH and Si-O-C bands after prolonged drying, we investigated the possibility that drying changes either Si_{2p} or O_{1s} signals. In deposited silane from a 2 percent concentration, O_{1s} shifted slightly (by 0.4 eV) to the higher energy side, while Si_{2p} had not changed its position at all. At least, with the ESCA instrument that we used, it is not easy to distinguish Si-O-Si from either Si-O-H or Si-O-C by Si_{2p} or O_{1s} signals. Bailey and Castle also found it difficult to resolve such differences by ESCA (24).

The thermal transition temperature of bulk, thick silane was analyzed by differential scanning calorimetry. As shown in Fig. 3, the glass transition of the aged, standard-dried sample (1 hour in the vacuum oven) is broader than for most polymers, with the T_g at about 52°C . The T_g is found to increase to 100°C and 108°C after drying at 110°C in a vacuum for 25 and 325 h

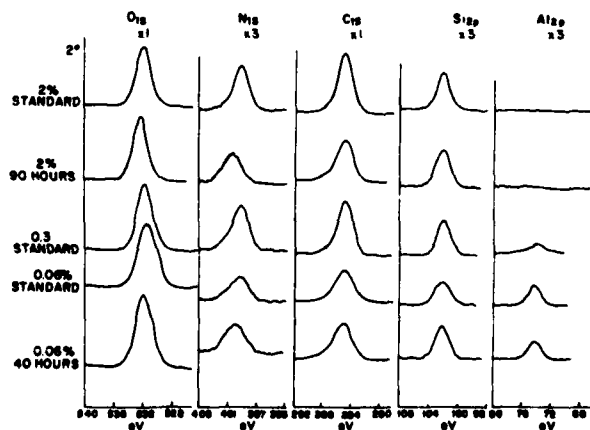


Fig. 2. ESCA scans of O, N, C, Si, and Al of deposited aminosilane.

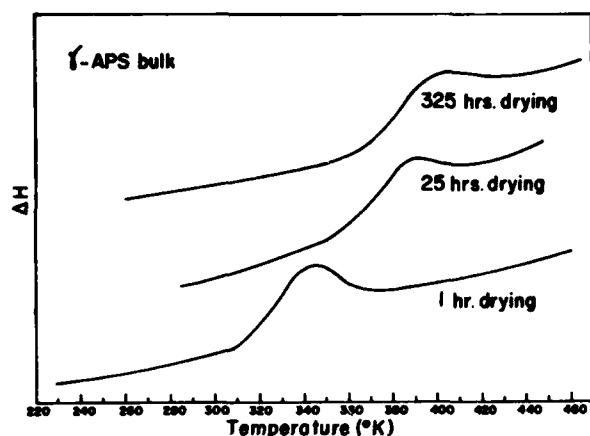


Fig. 3. DSC scans of γ -APS film as a function of drying at 110°C in a vacuum oven.

respectively. This trend supports increasing molecular weight and/or cross-linking in the silane bulk with extensive drying.

Evaluation of Joint Strength and Failure Surface Analysis

In order to correlate the structure of the deposited silane with joint strength, peel strength of the joint (sapphire/silane/polyethylene) was measured by a 180° peel test.

Peel strength, expressed in force/unit width of peeled surface, represents the total energy of fracture, consisting of the surface energy of the newly created surfaces and the energy spent for bulk deformation and plastic flow of the materials near the plane of separation. Due to the viscoelastic nature of polymers, peel strength, as measured, is strongly rate- and temperature-dependent, as investigated by Kaelble (25), Gent (26-29), and Andrews (30). Correlation of peel strength with interfacial adhesion strength, such as thermodynamic work of adhesion, is not always possible. Only when failure is a clean adhesive failure through the interface, can a meaningful correlation be made. It is, therefore, important to identify the failure mode and locus (31, 32). Under fixed test conditions (i.e., a constant peel rate, temperature, and geometry, as in our joint systems), any change in failure mode and locus with characteristic peel strength can be interpreted as a reflection of changes in the properties of the interfacial region.

Peel strength of PE/ γ -APS/sapphire joints is shown in Fig. 4 as a function of the concentration of γ -APS, used for spray-coating the sapphire plates. The joints were made after drying silane under standard conditions. A higher concentration means a thicker silane layer, with about 1000 Å corresponding to a 2 percent concentration. As shown in Fig. 4, a very low strength is observed when the sapphire is not treated with γ -APS. IR and ESCA analyses showed that the polyethylene that we used contained minimal amounts of carbonyl groups, and this seems to explain the low strength, since, in a PE/aluminum joint, Willis and Zichy (33) reported that peel strength increases with increasing amounts of carbonyl groups.

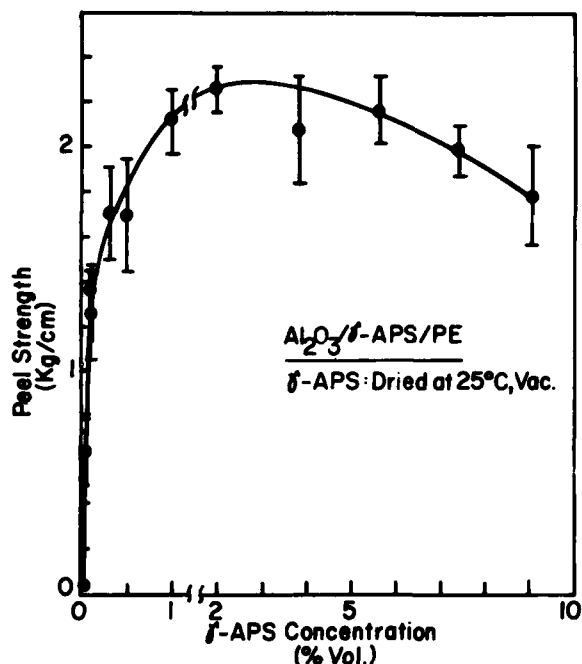


Fig. 4. 180° peel strength of α - Al_2O_3 / γ -APS/PE joint as a function of γ -APS concentration.

A sharp increase in peel strength is seen as silane is applied in increasing concentration, with a maximum strength of about 2.3 Kg/cm at 2 percent concentration. This maximum strength is at least seven times greater than the highest value reported with highly oxidized polyethylene and aluminum (33). A further increase in γ -APS concentration did not change the peel strength significantly. Low strengths observed with thin γ -APS films may not be attributable solely to the effects of thickness. In these thin silanes, the coverage shown by ESCA studies seems nonuniform, indicating weak spots contributing to the lower strengths.

Since chemical reaction is unlikely between γ -APS and the polyethylene that we used, which has few carbonyl groups, the interaction responsible for improved strength must be physical in nature. One possible interaction at the silane/polyethylene interface may be a limited interdiffusion. Such diffusion is feasible if γ -APS and polyethylene are at least partially compatible, since the joint is formed above the melting point of polyethylene (PE) and the T_g of γ -APS silane.

Thermal transition behavior, as studied by DSC, can provide useful insights into the miscibility question in blends of PE and silane. Figure 5 compares a DSC scan of the mixture of γ -APS and PE with that of unblended PE or γ -APS. Our sample of unblended PE shows a small T_g at -119°C and a T_m at 112°C , while unblended γ -APS (after 24 h of drying) shows a T_g at 100°C . In contrast, the mixture (about 50:50 by weight) exhibits a T_g at 32°C , which lies between the T_g 's of the unblended components. This T_g at 32°C must be due to the mixing of amorphous PE in silane. Whether another T_g is present in the mixture at a lower temperature cannot be conclusively ascertained because of the sensitivity limits of the instrument. When miscible, only one T_g is observed, while two T_g 's are observed if the blend has lim-

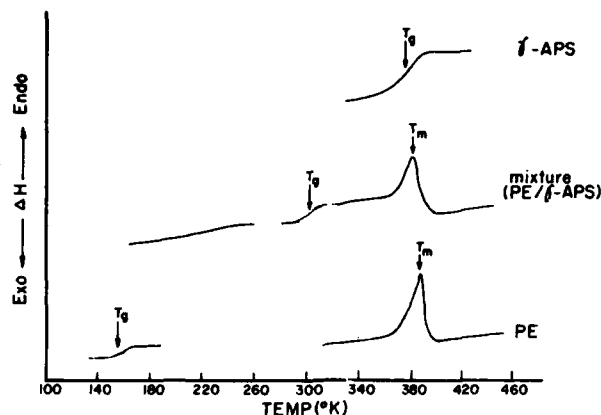


Fig. 5. DSC scans of unblended γ -APS (after drying at 110°C for 24 h), PE and the mixture of γ -APS and PE (~50:50 by weight) after heating at 150°C for 24 h.

ited miscibility. In cases where there are two T_g 's, the lower one would correspond to the amorphous PE-rich phase, while the higher T_g would correspond to the silane-rich phase. Even though we cannot distinguish between complete miscibility and limited miscibility, we may conclude that at least a partial miscibility exists in the mixture of γ -APS and PE. The mixture also shows a melting peak centered at 102°C, corresponding to the melting of crystallizable PE. This slight depression of the melting point from that of unblended components is often observed in other miscible polymer blends where one component is crystallizable (34). Therefore, the DSC results seem to indicate at least a partial miscibility of the amorphous PE and the silane polymer.

Another support for the compatibility of γ -APS and PE has been found by Schonhorn, *et al* (35), who utilized this compatibility to retain antioxidants (dissolved in γ -APS) from migrating to the surface of PE (36, 37).

In order to test the diffusion hypothesis, we have carried out several experiments. First, extensive drying of silane prior to joint formation leads to more polymerization and even to cross-linking, as supported by IR and thermal analyses. This may result in reduced diffusion and, thus, in lowering of joint strength, if diffusion is important. In Fig. 6, peel strength is plotted as a function of the drying time of silane, showing a decrease in peel strength with drying time in both concentrations. This result is not in conflict with our hypothesis. Secondly, the different degrees of interdiffusion may alter the structure and mechanical properties of the interfacial region and, thus, the failure mode. As exhibited by SEM studies of the peeled surfaces before extensive drying (Fig. 7), both fracture surfaces are rough as a result of the extensive plastic deformation and fibrillation of polyethylene, which is characteristic of cohesive failure of ductile polymers. With extensively dried silane (Fig. 8), both sides show smooth profiles, suggesting that the failure is close to adhesive failure. ESCA analyses of the fracture surfaces, as summarized in Table I, confirm the SEM results in that, in standard dried silane, only O_{1s} and C_{1s} peaks are observed on both sides, which suggests that the failure is cohesive through polyethylene. With the extensively dried

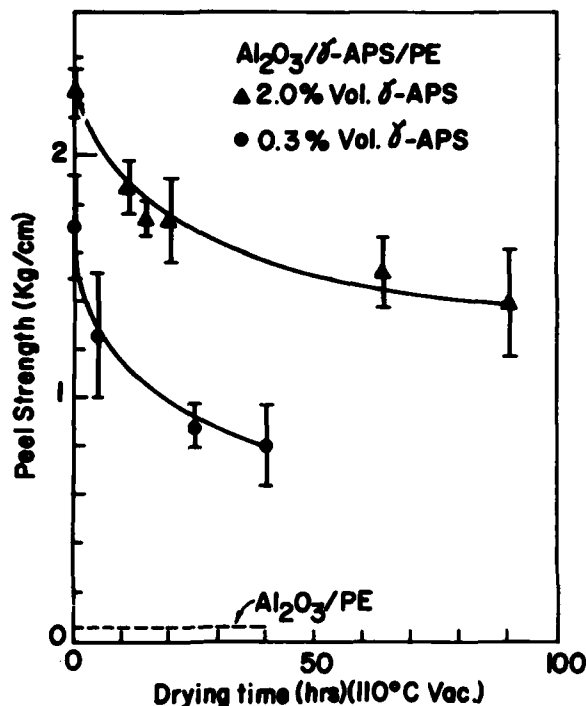


Fig. 6. 180° peel strength of α - Al_2O_3 / γ -APS/PE joint as a function of drying time at 110°C for γ -APS in a vacuum oven prior to joint formation.

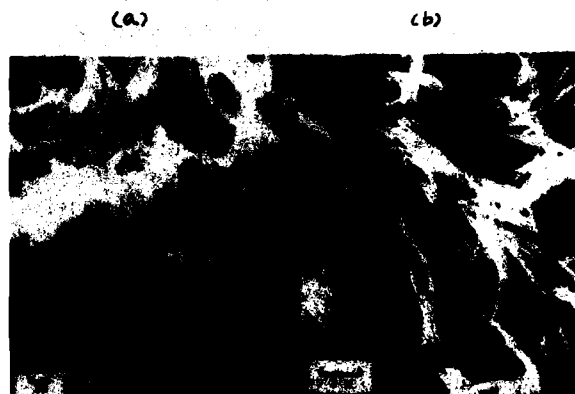


Fig. 7. Scanning electron micrograph of failure surfaces on (a) PE side and (b) α - Al_2O_3 side from α - Al_2O_3 / γ -APS/PE joints (γ -APS from 2 percent solution; joint formed with γ -APS dried at standard conditions).

silane, both N_{1s} and Si_{2p} peaks are also detected, as the failure is closer to adhesive failure through the interface. In the dried film, the relative intensities of N_{1s} and Si_{2p} peaks to the C_{1s} peak are much smaller than in the bulk silane, suggesting that the failure surfaces contain only a small fraction of silane. This may indicate that failure with the dried film took place near the silane/PE interface, probably as a mixed mode. Thus, results on failure surface analyses are also consistent with our hypothesis.

Characterization of γ -APS/Polyethylene Interface

Diffusion across the interface, in general, has been advocated by the Voyutskii and Vasenin school as an important mechanism for the autohesion of polymers (38-40). Vasenin has calculated that a diffusion layer of a

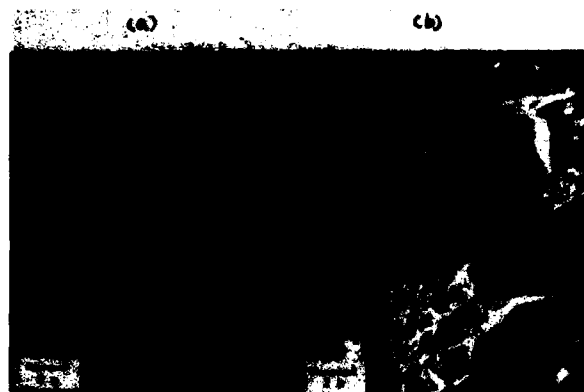


Fig. 8. Scanning electron micrograph of failure surfaces on (a) PE side and (b) α - Al_2O_3 side from α - Al_2O_3 / γ -APS/PE joints (γ -APS from 2 percent solution; joint formed with γ -APS dried at 110°C for 90 h).

very small thickness ($\sim 20 \text{ \AA}$) would be sufficient to increase peel strength significantly. Indeed, Jud and Kausch (41) recently found that a $20 \sim 30 \text{ \AA}$ depth of interpenetration will restore full materials properties in compatible polymers at temperatures near or slightly above T_g , as determined by fracture toughness measurements. Other recent evidence for diffusion was provided by directly measuring the concentration profile across the interface using an energy-dispersive X-ray microanalyzer attached to the SEM (SEM-EDX) (42, 43). SEM-EDX is a suitable technique in our systems, since the Si signal can be monitored across the interface to give a Si concentration profile. However, the spatial resolution in SEM-EDX is at best a fraction of a μ in distance, while, in our joint, the thickness of the silane is about 1000 \AA at a 2 percent concentration. Therefore, we made the laminate of polyethylene/ γ -APS/polyethylene by deliberately making the silane very thick (greater than 50μ). Conditions for drying the γ -APS film and the laminate were kept similar to those for the actual joint with sapphire. This laminate was then cut perpendicular to the interface, taking care not to contaminate the interface.

In SEM-EDX, there will be some smearing of each concentration measurement across the interface, since an electron has a finite mean free path within the polymeric material; X-rays are not generated at a unique point, but have a generation volume of about 1μ diame-

Table 1. ESCA Analyses on Failure Surfaces from Sapphire/ γ -APS/PE Joint

	Al_2O_3 Side		PE side	
	Standard Condition	Extensive Drying*	Standard Condition	Extensive Drying*
O_{1s}	533.1	533.1	533.1	533.1
N_{1s}	—	401.0	—	402.4
C_{1s}	285.9	285.9	286.0	286.2
Si_{2p}	—	102.6	—	104.2
Al_{2p}	—	—	—	—
O/C	0.04	0.07	0.12	0.14
Si/C	0	0.005	0	0.01

* 110°C , vacuum, 90 h.

*Si/C in deposited silane is $0.21 \sim 0.22$.

ter (42). This smearing problem must be assessed with a control sample where little or no diffusion occurs. Figure 9(a) illustrates the relatively sharp Si profile of a control sample of γ -APS film where no diffusion was expected. Another control sample of PE/ γ -APS/PE laminate was made under conditions where the extent of diffusion would be much less than for the regular laminates, since the time allowed for lamination was much shorter (3 min) at a lower temperature (121°C). Again, as shown in Fig. 9(a), the silicon concentration profile in this control sample is relatively sharp.

In comparison, Fig. 9(b) shows Si profiles as a function of drying time in PE/ γ -APS/PE laminates made under similar conditions to those of the actual joint with sapphire. It is obvious from Fig. 9(b) that the Si profiles are significantly broader than those of the control samples, but become sharper with extensively dried silane. These results provide evidence for the decreasing interdiffusion of γ -APS into polyethylene as the silane becomes more polymerized as a result of extensive drying.

We attempted to estimate the diffusion coefficients from Fig. 9(b), following the solution to the diffusion equation (42), which is applicable when the interface is much thinner than the thickness of the sample:

$$\frac{(C_1 + C_2) - 2C}{C_2 - C_1} = \text{erf} \frac{X}{2\sqrt{Dt}}$$

where C_1 is the minimum Si concentration, C_2 the maximum Si concentration, C is the Si concentration at position X , D is the diffusion coefficient, and t is the diffusion time. The plot of

$$\text{erf}^{-1} \frac{(C_1 + C_2) - 2C}{C_2 - C_1} \text{ vs. } X$$

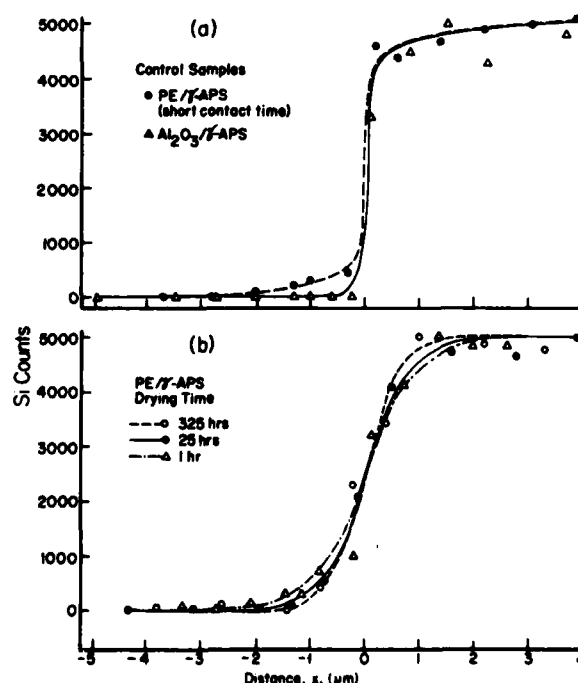


Fig. 9. Si concentration profile across the interface monitored by SEM-EDX in (a) control samples and (b) in PE/ γ -APS laminates as a function of drying time for γ -APS.

allows the estimation of D as a function of drying time, as shown in Fig. 10.

Table 2 summarizes the results on the diffusion coefficient, which is in the order of 10^{-12} cm²/s. For low-molecular-weight polyvinyl chloride or polycaprolactone, Gilmore, *et al* (43), obtained the same order of diffusion coefficient at a temperature about 30° above T_g . The diffusion constant, even after extensive drying, does not decrease more than 2.4 times, suggesting that the migration of low-molecular-weight silanes may be important in these measurements.

CONCLUSIONS

The following is a summary of the results obtained in this study.

- γ -aminopropyl triethoxy silane (γ -APS) forms a multimolecular film when adsorbed or deposited on an α -Al₂O₃ surface. The silane film is not fully cured when dried at room temperature for 1 h. Drying at elevated temperatures leads to further polymerization and possibly to cross-linking as evidenced by IR spectroscopy and thermal analyses, while prolonged drying may cause some degradation.
- The strength of the joint (α -Al₂O₃/ γ -APS/polyethylene) is improved markedly by the application of the γ -APS film, with maximum joint strength when the silane film is applied from a 2 percent aqueous solution.
- Drying the silane at elevated temperatures prior to joint formation reduces the joint strength and also changes the failure mode from cohesive failure through polyethylene to a mixed mode (cohesive and adhesive) near the interface.
- Evidence of interdiffusion between the γ -APS film and polyethylene at a temperature (149°C), which is above the melting point of polyethylene and the T_g of the silane film, was obtained by measuring the Si concentration profile across the interface of the laminate of polyethylene/ γ -APS/polyethylene. Diffusion constants in the order of 10^{-12} cm²/s were estimated, with a tendency toward reduced diffusion as a consequence of extensive drying. DSC results indi-

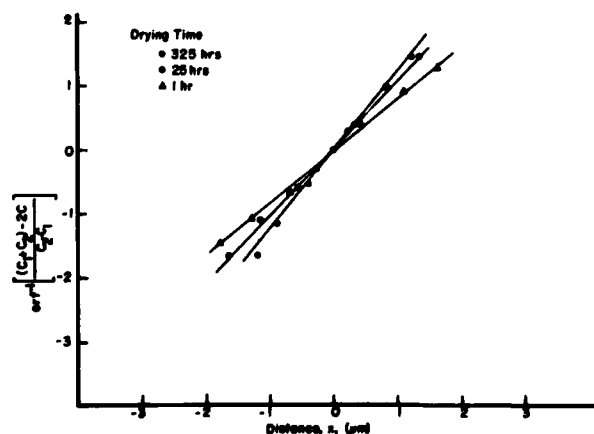


Fig. 10. Plot of $\text{erf}^{-1} \left[\frac{(C_1 + C_D) - 2C}{C_1 - C_1} \right]$ vs. X as a function of drying time for γ -APS.

Table 2. Estimated Diffusion Constant in γ -APS Film/PE Laminate

Drying time of γ -APS film* (h @ 110°C)	D^{**} (cm ² /s) $\times 10^{12}$
1	4.34
25	2.52
325	1.78

*prior to laminating with PE

**diffusion occurring at 148°C

cate at least partial miscibility of the silane polymer in the amorphous region of polyethylene.

In conclusion, our results strongly suggest that interdiffusion between (unoxidized) polyethylene and γ -APS silane film may be an important mechanism for the promotion of dry joint strength of a joint consisting of α -Al₂O₃/ γ -APS/polyethylene.

It will be useful to understand the possible interactions at the α -Al₂O₃/ γ -APS interface, and the joint strength in a wet environment. These will be the subject of future publications from our laboratory.

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